Thermodynamic Parameters for the Conformational Equilibrium of [Eu(tmhd)$_3$(3Me-py)$_2$] † from Slow-exchange Nuclear Magnetic Resonance Spectra ‡

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The low-temperature ^{1}H n.m.r. spectrum (<153 K) of [Eu(tmhd)$_3$(3Me-py)$_2$] has two peaks assigned to the picoline *ortho*-protons. This may be the result of either a Fermi contact interaction or the presence of unequally populated conformers related by rotation of the picoline ring about the Eu–N bond. The Fermi contact interaction is dismissed because the separation of the two *ortho* peaks of [Eu(tmhd)$_3$(3Me-py)$_2$] is solvent dependent, being 16 p.p.m. in CS_2 but only 3 p.p.m. in CCl_2F_2 at 153 K. The equilibrium constant for the conformational equilibrium has been calculated from the observed deviation of the two *ortho*, the *meta*, and the methyl peaks from the positions calculated assuming a dipolar mechanism. Analysis of the temperature dependence of the equilibrium constant yields values of $\Delta H^\ominus$ = 1.0 ± 0.2 kcal mol^{-1} and $\Delta S^\ominus$ = 8 ± 1 cal K^{-1} mol^{-1} in CCl_2F_2 and $\Delta H^\ominus$ = 4.3 ± 0.5 kcal mol^{-1} and $\Delta S^\ominus$ = 26 ± 3 cal K^{-1} mol^{-1} in CS_2. The large values for $\Delta H^\ominus$ and $\Delta S^\ominus$ observed in CS_2 suggest that solvation plays a dominant role in the conformational equilibrium. The smaller values observed in CCl_2F_2 indicate that solvation is less important there, but the relatively large $\Delta S^\ominus$ shows that it remains a significant factor.

EARLY in our investigation of the shifts induced by [Eu(tmhd)$_3$] in the ^{1}H n.m.r. spectrum of the unsymmetrical 3-picoline (3-methylpyridine, 3Me-py) molecule we reported [1,2] that at low temperatures in the slow intermolecular exchange region (< −120 °C) there were two *ortho* signals, but only single peaks for each of the *meta*-, *para*-, and methyl protons, as well as single resonances for the t-butyl and methine protons of the tmhd chelates. We first interpreted this doubling of the *ortho* peaks as evidence for restricted rotation about the Eu–N bond. This idea was plausible since the *X*-ray structure of [Eu(tmhd)$_3$(py)$_2$] had revealed that each pyridine ring experienced 11 intramolecular van der Waals contacts.[3,4] Furthermore, as the temperature of the original sample was decreased, we observed the appearance of two signals, in the region assigned to coordinated picoline methyl resonances, separated by 280 Hz at −115 °C. From this we set a lower limit of 7 kcal mol^{-1} on the barrier to rotation.[5,§]

Later, superior low-temperature spectra of various symmetrical pyridine derivatives, *i.e.* pyridine, 4-picoline (4-methylpyridine), and 3,5-lutidine (3,5-dimethylpyridine, 3,5Me$_2$-py), obtained on a Varian XL-100 n.m.r. spectrometer, exhibited single *ortho*, *meta*, and methyl resonances.[6] In addition we were unable to reproduce the splitting of the 3Me-py methyl resonances observed in our original experiment in either CS_2 or CCl_2F_2 when stringent inert-atmosphere precautions were maintained. However, when we examined the n.m.r. spectra of several samples which had been stored outside the inert-atmosphere box for more than a day or two we saw a second peak in the vicinity of the 3Me-py methyl resonance. We now suspect that this peak is due to the presence of water which the samples presumably absorbed on standing.

Since the rotational barrier about the Eu–N bond should be at least as large in [Eu(tmhd)$_3$(3,5Me$_2$-py)$_2$] as in [Eu(tmhd)$_3$(3Me-py)$_2$], and since we obtained no evidence for such a barrier with 3,5Me$_2$-py, or any symmetrical pyridine, it was apparent that the pair of *ortho* signals observed for 3Me-py must arise from some other phenomena. We know of two possible mechanisms which could produce the observed splitting of the *ortho* resonance. These are a Fermi contact shift or the presence of rapidly interconverting, unequally populated, conformers resulting from pyridine-ring rotation. In this paper we present evidence that the latter mechanism is responsible for our observations, and we determine approximate thermodynamic parameters for the rotational equilibrium in two solvents.

METHODS AND RESULTS

N.m.r. samples containing [Eu(tmhd)$_3$] and either 3Me-py or 3,5Me$_2$-py were prepared in CCl_2F_2 or CS_2 and spectra were obtained as previously described.[6] The isotropic shifts derived from these spectra in CCl_2F_2 at various temperatures are listed in Table 1.

Our earlier work with substituted-pyridine adducts of [Eu(tmhd)$_3$] indicates that all of these compounds have the basic [Eu(tmhd)$_3$(py)$_2$] [3,4] structure. If an unsymmetrical heterocycle such as 3Me-py is substituted into this structure, the isomers illustrated as AA and BB in Figures 1 and 2 can result. A third isomer, in which the two-fold axis is absent, due to differing orientations of the 3Me-py ring, *i.e.* an AB isomer, is also possible. However, we assume that the n.m.r. shifts of one picoline ring are insensitive to the orientation of the other. Thus the isotropic shifts are only a function of the total number of picolines in the A and B conformational orientations, so that we can obtain the A : B ratio but we cannot obtain any information about the distribution of the AA, AB, and BB isomers. Since the steric interactions of the picoline methyl group with the chelated tmhd ligands vary in the A and B conformational

† Bis(3-methylpyridine)tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III).

‡ This paper is abstracted in part from a dissertation submitted to the Graduate Division of the University of Hawaii by R. D. in partial fulfilment of the requirements for the Doctor of Philosophy Degree in Chemistry, August 1975.

§ Throughout this paper: 1 cal = 4.184 J.

TABLE 1

Isotropic shifts (p.p.m.), magnetic parameters (D), and agreement factors (R) for [Eu(tmhd)$_3$(3Me-py)$_2$] and [Eu(tmhd)$_3$-(3,5Me$_2$-py)$_2$] at several temperatures in CCl_2F_2

	T = 143 K			T = 139 K			T = 135 K		
	3,5Me$_2$-py		3Me-py	3,5Me$_2$-py		3Me-py	3,5Me$_2$-py		3Me-py
	obs.	calc.	obs.	obs.	calc.	obs.	obs.	calc.	obs.
ortho	−67.73	−67.35	−73.76	−69.33	−69.33	−75.12	−70.74	−70.37	−79.67, −70.22
meta			−26.56			−27.12			−27.62
para	−21.19	−21.53	−23.27	−21.99	−22.17	−23.32	−22.40	−22.93	−23.57
3-methyl	−14.26	−14.21	−15.30	−14.97	−14.57	−15.48	−15.50	−14.89	−15.64
t-butyl	8.81	9.77	8.97	8.81	10.04	9.15	8.99	10.11	9.33
methine	28.42	28.75	31.14	31.08	30.73	31.67	31.79	32.15	32.38
D_1 (σ)	1 613 (113)			1 739 (132)			1 775 (140)		
D_2 (σ)	−6 030 (325)			−6 131 (383)			−6 357 (413)		
R	0.015			0.017			0.018		

	T = 131 K			T = 127 K			T = 123 K		
	3,5Me$_2$-py		3Me-py	3,5Me$_2$-py		3Me-py	3,5Me$_2$-py		3Me-py
	obs.	calc.	obs.	obs.	calc.	obs.	obs.	calc.	obs.
ortho	−73.76	−73.92	−81.55, −70.90	−75.37	−74.96	−84.29, −72.04	n.o.		−86.49 −72.49
meta			−28.15			−29.04			−29.57
para	−23.41	−23.60	−23.93	−23.76	−24.38	−24.46	n.o.		−24.82
3-methyl	−16.21	−15.52	−15.82	−16.57	−15.84	−16.00	n.o		−16.17
t-butyl	9.35	10.71	9.50	9.35	10.78	9.60	n.o.		9.68
methine	33.38	32.77	33.98	33.92	34.26	34.87	n.o.		35.04
D_1 (σ)	1 857 (143)			1 899 (170)			1 967 *		
D_2 (σ)	−6 627 (424)			−6 750 (504)			−6 971 *		
R	0.018			0.020					

n.o. = not observed. * Extrapolated value.

orientations, they will have unequal populations determined by the equilibrium constant $K = [A]/[B]$. Thus, although fast exchange still occurs, the two different *ortho* protons [*i.e.* H(2) and H(6)] do not spend an equivalent amount of time in each environment and thus experience different isotropic shifts. The situation is analogous to $[Ni(en)_3]^{2+}$ (en = ethylenediamine) where two CH_2 peaks are observed due to the unequal population of the rapidly interconverting δ and λ ring conformers.[7]

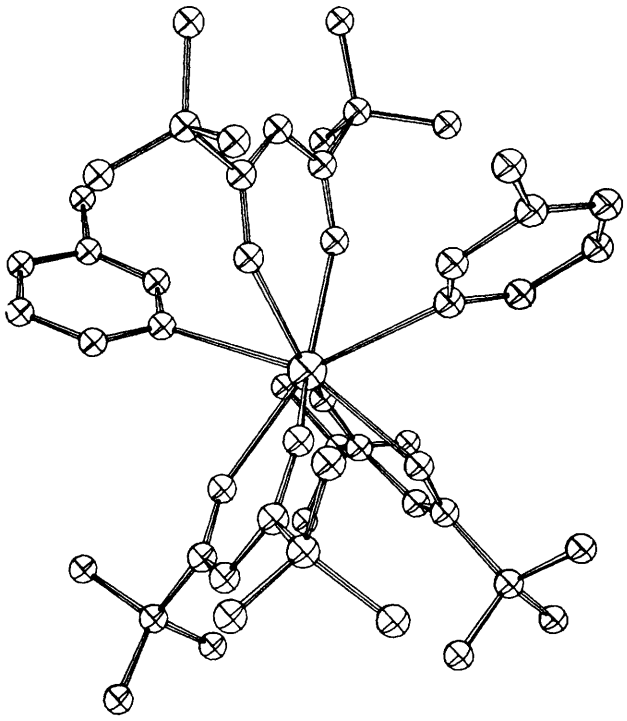

FIGURE 1 The AA isomer of [Eu(tmhd)$_3$(3Me-py)$_2$]

Since the shifts of all of the protons of the AA and BB isomers can be accurately calculated using the methods previously described,[1,2,6] it is possible to determine the equilibrium constant, K. In order to do so it is necessary to know the isotropic shifts of each of the protons of the individual 3-picoline conformational orientations. These can be calculated from equation (1) if we know the magnetic anisotropy parameters D_1 and

$$\Delta\nu/\nu_0 = D_1[G(\theta,r)] + D_2[G(\theta,\Omega,r)] \quad (1)$$

D_2 and the geometric parameters $G(\theta,r)$ and $G(\theta,\Omega,r)$. Using the observed 3,5-lutidine isotropic shifts, the known structure of $[Eu(tmhd)_3(py)_2]$,[3,4] and the full two-term dipolar-shift equation (1), we calculated[2,6] the magnetic anisotropy parameters D_1 and D_2 as summarized in Table 1 for each temperature. Since D_1 and D_2 are insensitive to substitution of the pyridine ring,[6]

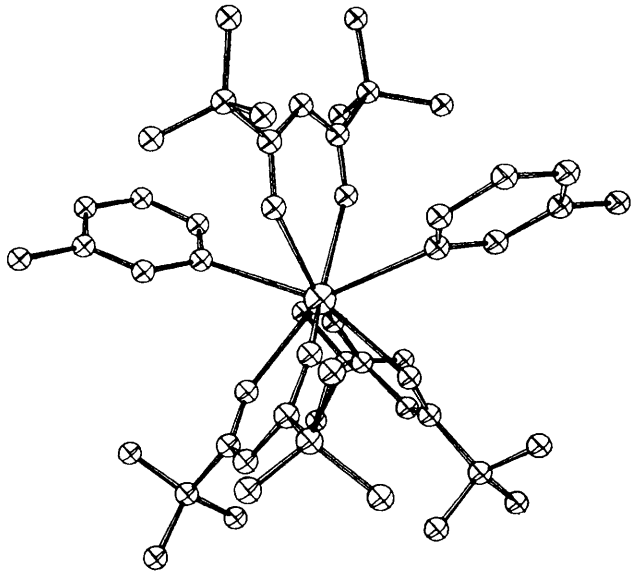

FIGURE 2 The BB isomer of $[Eu(tmhd)_3(3Me\text{-}py)_2]$

these magnetic anisotropy parameters were then applied to the $[Eu(tmhd)_3(3Me\text{-}py)_2]$ molecule. The geometric factors were calculated for the two 3-picoline conformational orientations assuming they were locked into the orientation found for the pyridine rings in $[Eu(tmhd)_3(py)_2]$.[3,4] Since differences in the overall structures of the three isomers of $[Eu(tmhd)_3(3Me\text{-}py)_2]$ are likely to be small, it is reasonable to assume that nearly identical geometric factors apply for each equivalent site, *i.e.* as in (2) and (3).

$$G(\theta,r)_{AA} = G(\theta,r)_{BB} = G(\theta,r)_{AB} \quad (2)$$

$$G(\theta,\Omega,r)_{AA} = G(\theta,\Omega,r)_{BB} = G(\theta,\Omega,r)_{AB} \quad (3)$$

Under this assumption, in the absence of exchange between isomers, one *para*, two *meta*, two picoline methyl, and two *ortho* signals would be observed at positions calculated *via* equation (1). However, even though intermolecular exchange is slow at low temperature, the complex is fluxional as evidenced by the single t-butyl and methine tmhd chelate peaks. Thus there is some intramolecular process which exchanges the isomers and averages the shifts of the conformational orientations. We can therefore write (4) for the picoline methyl isotropic shift where $\Delta\nu_{CH_3}$(obs.) is the observed

$$\Delta\nu_{CH_3}(\text{obs.}) = \tau_A\Delta\nu_{CH_3}(A) + \tau_B\Delta\nu_{CH_3}(B) \quad (4)$$

picoline methyl isotropic shift, $\Delta\nu_{CH_3}(A)$ and $\Delta\nu_{CH_3}(B)$ are the calculated picoline methyl isotropic shifts for the A and B conformational orientations respectively, and τ_A and τ_B are the fractional populations of the A and B sites. Since $\tau_A = 1 - \tau_B$ the only unknown in (4) is τ_A which may be calculated. The equilibrium constant may then be obtained from (5). The *meta*-proton experiences

$$K = \tau_A/\tau_B \quad (5)$$

similar behaviour and can be treated in an analogous fashion to yield an independent value for K. The *para*-proton has the same calculated isotropic shift in both the A and B conformational orientations and yields no information about the conformational equilibria.

For the *ortho*-protons, the assumptions behind equations (2) and (3) will cause the *isotropic* shifts to be equal [equations (6) and (7)], where $\Delta\nu_2(A)$ is the isotropic shift for the H(2) proton in the A conformational orientation and the other symbols are defined in a similar manner. Upon accounting for exchange between isomers the observed shift for H(2) will be as in (8) and

$$\Delta\nu_2 = \Delta\nu_6(B) \quad (6)$$

$$\Delta\nu_6(A) = \Delta\nu_2(B) \quad (7)$$

$$\Delta\nu_2(\text{obs.}) = \tau_A\Delta\nu_2(A) + \tau_B\Delta\nu_2(B) \quad (8)$$

similarly for H(6) [equation (9)]. Substituting (6) and

$$\Delta\nu_6(\text{obs.}) = \tau_A\Delta\nu_6(A) + \tau_B\Delta\nu_6(B) \quad (9)$$

(7) into (9) we have (10). From equations (8) and (10)

$$\Delta\nu_6(\text{obs.}) = \tau_A\Delta\nu_2(B) + \tau_B\Delta\nu_2(A) \quad (10)$$

two more independent determinations of K result. Examples of data used and the resulting K values for two sets of conditions can be found in Table 2.

TABLE 2

Examples of data (p.p.m.) used to determine K for $[Eu(tmhd)_3(3Me\text{-}py)_2]$

Position	Calc. $\Delta\nu$ for A*	Observed $\Delta\nu$	Calc. $\Delta\nu$ for B*	K
		CCl_2F_2, $T = 131$ K		
H(2)	−28.08	−81.55	−121.03	0.74
H(6)	−121.03	−70.90	−28.08	0.85
H(5)	−36.24	−28.15	−20.90	0.90
3-CH_3	−9.25	−15.82	−22.15	0.96
		CS_2, $T = 154$ K		
H(2)	−41.88	−76.4	−95.20	0.54
H(6)	−95.20	−60.8	−41.88	0.54
H(5)	−30.38	−23.4	−21.49	0.27
3-CH_3	−10.57	−15.3	−17.81	0.54

* Calculated with D_1 and D_2 obtained for $[Eu(tmhd)_3(3,5Me_2\text{-}py)_2]$ and structure of $[Eu(tmhd)_3(py)_2]$, see text.

Upon changing the temperature, the magnetic parameters D_1 and D_2 in equation (1) and the equilibrium constant K change. New values for D_1 and D_2 can be determined from the analysis of the 3,5Me_2-py data and using these values the new equilibrium constant can be determined *via* the method outlined above. This process can be repeated at several different temperatures and thus the temperature dependence of the equilibrium constant and thermodynamic parameters can be obtained. Figure 3 is a representative plot of ln$K$ against $1/T$ from an analysis of the data for the *meta*- and methyl protons of 3-picoline in CCl_2F_2. Table 3

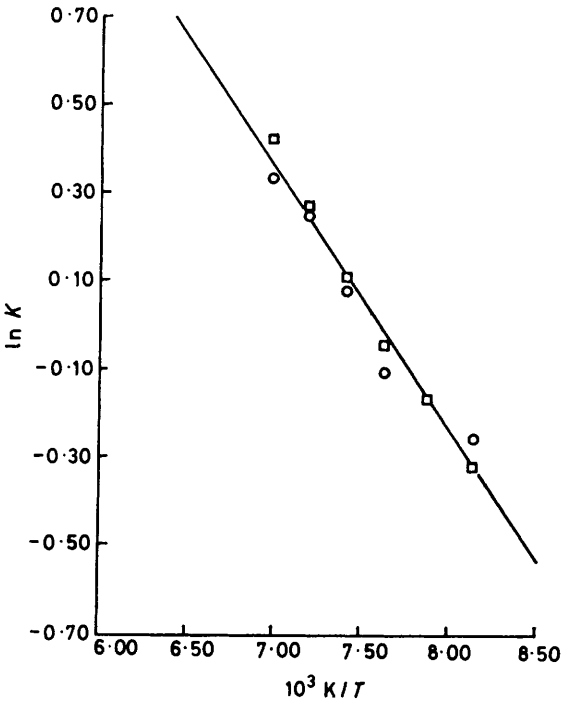

FIGURE 3 Plot of ln K against $1/T$ for [Eu(tmhd)$_3$(3Me-py)$_2$] in CCl_2F_2. The circles represent data from the *meta*-proton and the squares from the picoline methyl signal

summarizes the least-squares results of such plots obtained from the 3-picoline methyl, *meta*, and *ortho* data.

The resulting average $\Delta H^\ominus$ and $\Delta S^\ominus$ values for the A ⟶ B conformational conversion are 1.0 ± 0.2 kcal mol^{-1} and 8 ± 1 cal K^{-1} mol^{-1} respectively, in CCl_2F_2 and 4.3 ± 0.5 kcal mol^{-1} and 26 ± 3 cal K^{-1} mol^{-1} respectively in CS_2. Comparison of these values with the corresponding thermodynamic parameters obtained from treatment of the 3Me-py methyl, *meta*, and *ortho* data reveals that they all lie within 2σ of each other. Considering the large number of uncertainties encountered in this investigation (*i.e.* the narrow temperature range in which experimental data were available, probable contact contamination of the lanthanoid shifts, and the multistep procedure required to obtain the thermodynamic data) the scatter of the values in Table 3 is to be expected.

TABLE 3

Summary of least-squares analysis of ln K against $1/T$ plots for the picoline methyl, *meta*, and *ortho* data for [Eu(tmhd)$_3$(3Me-py)$_2$]

Assignment	No. of points	Temperature range (K)	$\Delta H^\ominus(\sigma)$ * kcal mol^{-1}	$\Delta S^\ominus(\sigma)$ * cal K^{-1} mol^{-1}
		CCl_2F_2		
ortho	6	123—144	1.2 (1)	10 (1)
meta	5	123—144	1.2 (2)	8 (1)
Methyl	6	123—144	0.8 (2)	6 (1)
Average			1.0 (2)	8 (1)
		CS_2		
ortho	3	154—160	5.6 (8)	35 (6)
meta	3	158—160	3.4 (5)	19 (4)
Methyl	3	154—160	4.0 (2)	25 (2)
Average			4.3 (5)	26 (3)

* Standard deviation.

DISCUSSION

In an unsymmetrically substituted pyridine such as 3Me-py the chemical shifts of the two *ortho*-protons are different. In a diamagnetic system this difference is only a few tenths of a p.p.m. compared to the shift separation of 16 p.p.m. observed for [Eu(tmhd)$_3$(3Me-py)$_2$] at 153 K in CS_2. Shift reagents do not simply multiply chemical shifts but rather add a new chemical-shift term. In a fluxional molecule, the dipolar mechanism cannot lead to two different *ortho* shifts if the A and B conformational orientations are equally populated. The observation of two resonances from *ortho*-protons thus implies the presence of a Fermi contact shift, or an unequal population of the A and B conformational orientations.

The strongest evidence against rationalization of our results in terms of the Fermi contact shift is the observed solvent dependence of the separation between the *ortho* peaks. The separation of the two *ortho* peaks in [Eu(tmhd)$_3$(3Me-py)$_2$], is 16 p.p.m. in CS_2 but only 3 p.p.m. in CCl_2F_2 at 153 K.* Examination of the contact-shift equation [8] reveals no parameters directly dependent on solvent, *i.e.* viscosity or dielectric constant, but only parameters related to the electronic and nuclear properties of the complex. Therefore contact shifts show little or no solvent dependence, and are not likely to be the cause of the phenomena reported here.

The fact that reasonable and consistent thermodynamic values are obtained also supports the unequally populated conformational model over the Fermi contact model. The fact that the treatment is successful and that the $\Delta H^\ominus$ and $\Delta S^\ominus$ values obtained from the picoline methyl, *meta*, and *ortho* data agree with each other

* At 153 K in CS_2, two *ortho* signals separated by 16 p.p.m. are observed. In CCl_2F_2 at this temperature, the system is still in the intermediate intermolecular-exchange region. Two *ortho* peaks are not observed in CCl_2F_2 until the temperature is lowered to 135 K at which temperature they are separated by 10 p.p.m. If a plot of shift against temperature is extrapolated to 153 K the two *ortho* peaks would be separated by only 3 p.p.m., *i.e.* they would be too close to be resolved and would be observed as a single peak.

strongly implies the existence of unequally populated conformational orientations.

Since both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are positive there will be a temperature at which $\Delta G^{\ominus} = 0$ and $K = 1$. At this temperature both conformational orientations have the same population and $\tau_A = \tau_B = 0.5$. Substitution of these values into equations (8) and (10) shows that $\Delta\nu_2$(obs.) = $\Delta\nu_6$(obs.) under these conditions, *i.e.* ν_2 and ν_6 become isochronous. Using the average values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ in Table 3 we find $\Delta G^{\ominus} = 0$ at 131 K in CCl_2F_2. Experimentally we observe a single *ortho* resonance at 143 K, at which temperature the spectra of [Eu(tmhd)$_3$(3Me-py)$_2$] and 3Me-py are first resolved (see Figure 4). This single resonance is also seen at 139 K, but upon cooling to 135 K it splits into two resonances which spread apart as the temperature is decreased. Considering the uncertainties involved in obtaining $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$, the calculated temperature, 131 K, at

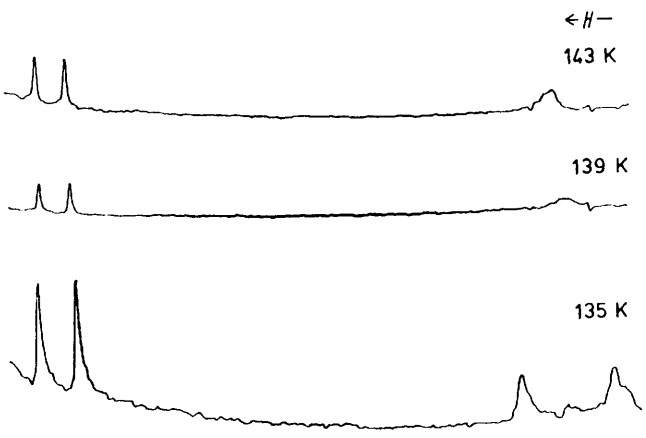

FIGURE 4 N.m.r. spectra (100 MHz) of [Eu(tmhd)$_3$(3Me-py)$_2$] in CCl_2F_2. The peaks are from high to low field, *para*, *meta*, and *ortho*. See Table 1 for isotropic shifts

which $\Delta G^{\ominus} = 0$ is in good agreement with the experimental result which indicates that $\Delta G^{\ominus} \approx 0$ over the range 135—143 K. The unequally populated conformational orientation model is thus able to explain the behaviour of the *ortho* peaks over the observed temperature range. If the separation of the *ortho* peaks were due to the Fermi contact shift one would not expect to observe only one peak at any temperature.

The temperature at which $\Delta G^{\ominus} = 0$ in CS_2 is calculated to be 166 K which lies in the intermediate intermolecular-exchange region in that solvent. Signals due to [Eu(tmhd)$_3$(3Me-py)$_2$] and 3Me-py are not resolved until 160 K at which point only one *ortho* peak is observed at a chemical shift within 6% of that expected for a 50% population of each conformational orientation. This peak splits into two at 156 K, so that again the observation is in accord with the thermodynamic values.

Further experimental evidence for our model results from a comparison of the isotropic shifts of the 3-methyl protons of 3Me-py and the 3,5-methyl protons of 3,5-Me$_2$-py. In general the isotropic shifts of [Eu(tmhd)$_3$(3,5Me$_2$-py)$_2$] are smaller than those for [Eu(tmhd)$_3$(3Me-py)$_2$], see Table 1. However, the methyl shift for 3Me-py is larger than the corresponding shift for [Eu(tmhd)$_3$(3,5Me$_2$-py)$_2$] at the three highest temperatures in Table 1 and smaller for the three lowest temperatures. Since 3,5Me$_2$-py has two methyl groups and no conformational preference, its shifts always represent a 50% contribution from the A and B conformational orientations, and therefore lie at the midpoint between the shifts calculated for these orientations. Figure 3 shows that for the three highest temperatures $\ln K > 0$ and $\Delta G^{\ominus} < 0$ which means that the A conformational orientation is more populated than the B. Since the picoline methyl shift is greater in the A conformational orientation the observed picoline CH_3 shift of [Eu(tmhd)$_3$(3Me-py)$_2$] is therefore larger than that of the lutidine CH_3 shift of [Eu(tmhd)$_3$(3,5Me$_2$-py)$_2$]. At the three lower temperatures $\ln K < 0$ and $\Delta G^{\ominus} > 0$ so that the B conformational orientation is more populated than the A. Therefore the observed shift of the 3Me-py methyl group of [Eu(tmhd)$_3$(3Me-py)$_2$] at these temperatures becomes smaller than that of the corresponding group in the [Eu(tmhd)$_3$(3,5Me$_2$-py)$_2$] complex. When $\Delta G^{\ominus} = 0$, the 3Me-py methyl shift should equal the 3,5Me$_2$-py shift. As stated above, this temperature is calculated to be 131 K while the shifts are observed to become equal somewhere in the 131—135 K range. Thus the unequally populated conformational orientation model quantitatively accounts for the observed behaviour of the 3Me-py methyl shift relative to that of the 3,5Me$_2$-py methyl shift.

The errors for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ in CS_2 are higher than the corresponding values in CCl_2F_2 due to the very limited temperature range, 5 K, available between coalescence and the freezing point in CS_2. Nevertheless the values obtained in CS_2 are interesting, in spite of the relatively high errors. The values for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are too large to be accounted for by differing steric interactions between picoline, methyl, and the chelate in the two conformational orientations. Instead they suggest that a CS_2 molecule is associated with the [Eu(tmhd)$_3$(3Me-py)$_2$] molecule in one of the conformational orientations, but is lost in the other. The CS_2 could be involved in a base-stacking interaction with either the pyridine ring or the diketonate in one conformational orientation but displaced due to steric constraints in the other. An energy of *ca.* 4 kcal mol^{-1} is reasonable for such a base-stacking interaction and the displacement of a molecule would lead to a $\Delta S^{\ominus}$ value of *ca.* 20 cal K^{-1} mol^{-1}.

The smaller $\Delta H^{\ominus}$ value observed in CCl_2F_2 could arise from simple steric differences between the two conformational orientations. However the $\Delta S^{\ominus}$ value is too large to be accounted for by the simple conformational difference and indicates that solvation also plays some role. We note that San Filippo, jun., *et al.*[9] recently reported that alkyl fluorides co-ordinate to lanthanoid shift reagents in a fashion similar to organic substrates containing much more basic heteroatom centres.

Lately, several other workers have reported stereoselective interactions of lanthanoid shift reagents with

unsymmetrical ketones.[10-12] Such ketones differ from 3Me-py in that they have two different lone pairs on the ketone oxygen at which co-ordination of the lanthanoid may occur while 3Me-py has only one co-ordination site. However, in both cases the result is that the observed lanthanoid-induced shifts (LIS) are a weighted average of the shifts characteristic of the non-equivalent sites. The necessity of accounting for such isomers in the calculation of LIS has been pointed out.[12] Lenkinski and Reuben [12] were able to obtain the population of the two sites in unsymmetrical ketones but did not determine thermodynamic parameters for the equilibrium between them.

The data reported by Davis and Willcott [13] for the [Yb(tmhd)$_3$]–3-fluoropyridine system indicates that unequal populations of rotational conformers also exist in that system. They observed two signals differing by several p.p.m. for the *ortho*-^{13}C, *ortho*-^{1}H, and *meta*-^{13}C which are in accord with our conclusions in this study. Since the conformational behaviour of the [Ln(tmhd)$_3$]–3-fluoropyridine complex was not considered in their study, a systematic error is present in their analysis of the contact shifts in that system. This probably does not effect their conclusions but it may introduce considerable error into the values they deduce for the contact shift.

Conclusion.—This investigation presents experimental evidence for the existence of unequally populated conformers in complexes formed by shift reagents and their adducts. While some workers [14,15] have suggested that shift reagents exist in solution as an ensemble of many rapidly interconverting geometrical isomers, no one has yet postulated the existence of one geometrical isomer whose structure rapidly equilibrates between several conformers. Our success in obtaining thermodynamic parameters describing a conformational equilibrium supports the idea that [Eu(tmhd)$_3$(py)$_2$] exists in solution as a fluxional molecule whose basic structure is that found in the solid state. These results provide strong evidence that the bis(pyridine) adducts of [Eu(tmhd)$_3$] do *not* exist in solution as an ensemble of many rapidly interconverting geometrical isomers with each isomer having its own susceptibility tensor,[15] but rather as a molecule rapidly interconverting between two conformational orientations which have the same basic structure and with susceptibility tensors which are in accord with those measured in the solid state.[14,16]

The fact that conformational restrictions apparently occur with relatively small substrates such as 3-picoline indicates that they will be the rule rather than the exception. If such is the case, then in order to adequately explain lanthanoid induced shifts, a method of accurately selecting populated conformations of the complex must be found.

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